EXHIBIT B

RUTGERS

PCBs in pigments, inks, and dyes: Documenting the problem

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June 19, 2013

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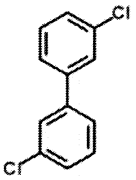
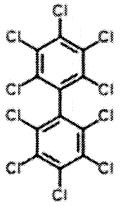
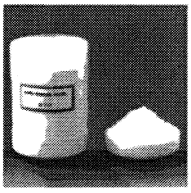
Known inadvertent PCB sources

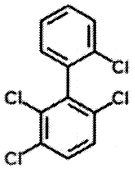
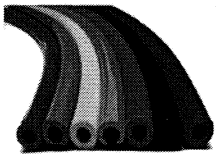
- Organic pigments, especially diarylide yellow, produce primarily PCB 11, among others




- Titanium dioxide (inorganic white pigment) produces PCBs 206, 208, and 209

- Silicone rubber tubing produces PCBs 44 and 45, among others (don't use for PCB sampling!)

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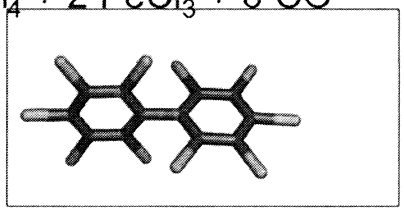
PCBs 206, 208, 209

Produced inadvertently during the making of titanium tetrachloride

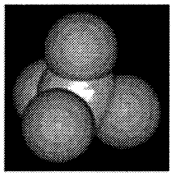
Often sold to water treatment plants as a flocculant

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$

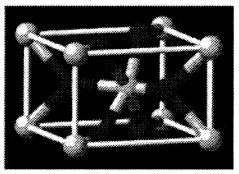
This carbon is chlorinated to form PCBs



Most $TiCl_4$ is then used to make TiO_2 (white pigment)



$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$



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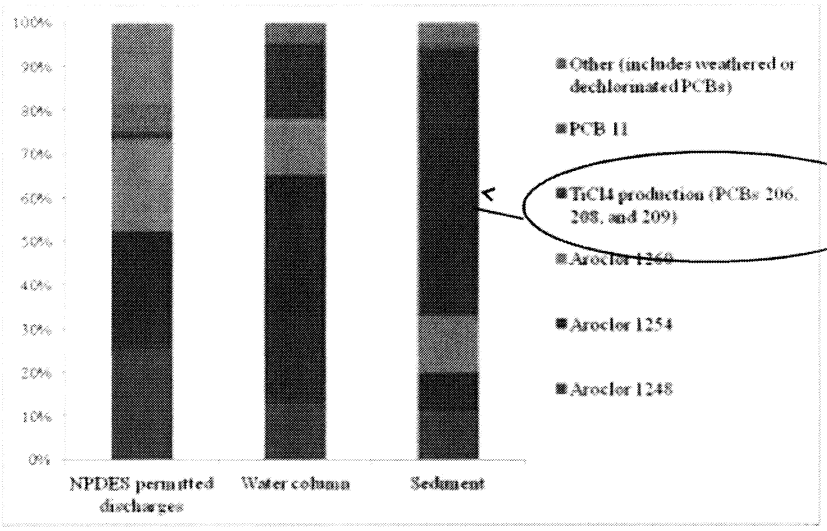
PCBs from TiO_2 production in Wilmington, DE, contribute 61% of all PCBs in surface sediment in the Delaware River



(Praipipat *et al.*, 2013 ES&T)

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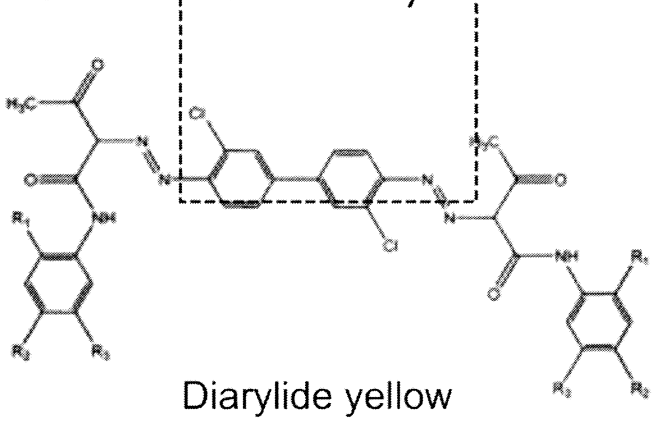
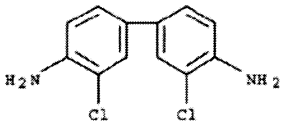
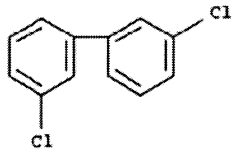
PCB 11 from Diarylide Yellows



Diarylide yellow



3,3'-dichlorobenzidine



PCB 11 (3,3'-diCB)

R_1,R_2,R_3 = H	Pigment yellow 12
R_1,R_2 = CH_3, R_3 = H	Pigment yellow 13
R_1 = OCH_3, R_2, R_3 = H	Pigment yellow 17
R_1,R_3 = OCH_3, R_2 = Cl	Pigment yellow 83

(Basu *et al.*, 2009)

- All listed in EPA's Toxic Substances Control Act (TSCA) inventory

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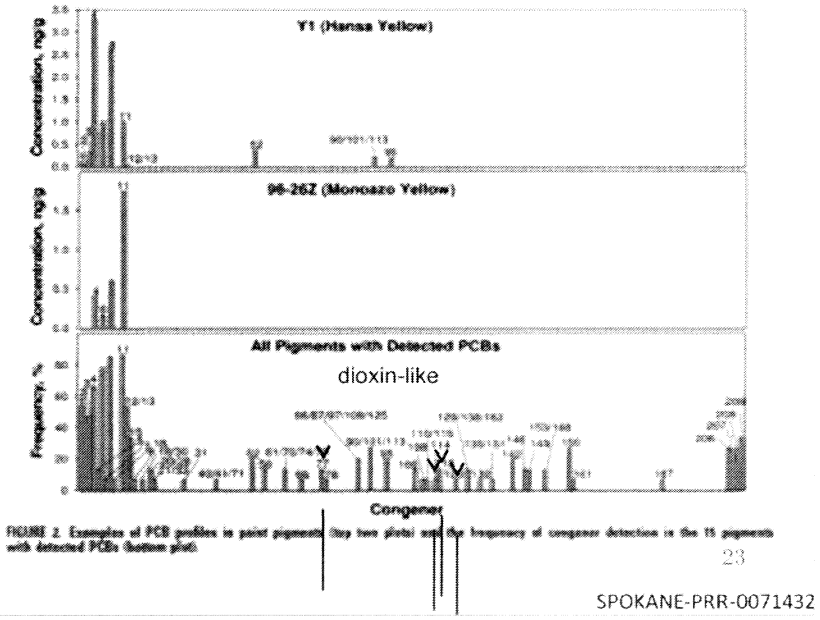
Other PCBs in pigments

From Hu and Hornbuckle, 2010 ES&T

Simon Litten also found (dioxin-like) PCB 77 in pigment process waste, TEQ = 0.0001 (Litten *et al.*, 2002)



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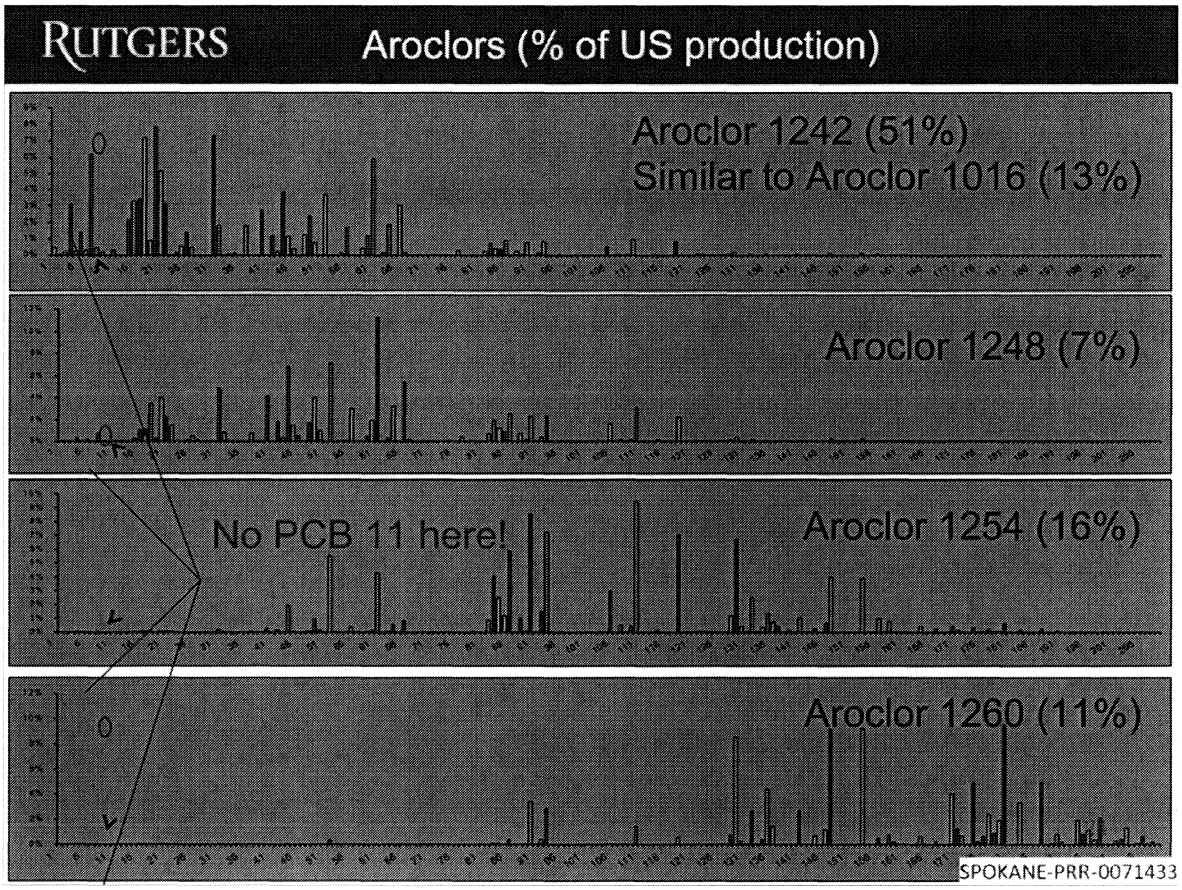
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Aroclors (% of US production)
Aroclor 1242 (51%)
Similar to Aroclor 1016 (13%)
Aroclor 1248 (7%)
No PCB 11 here!
Aroclor 1254 (16%)
Aroclor 1260 (11%)
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TSCA contains a loophole allowing for inadvertent production of PCBs

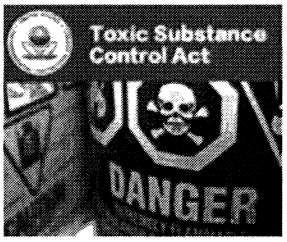
Under TSCA, the inadvertent production of PCBs is allowed.

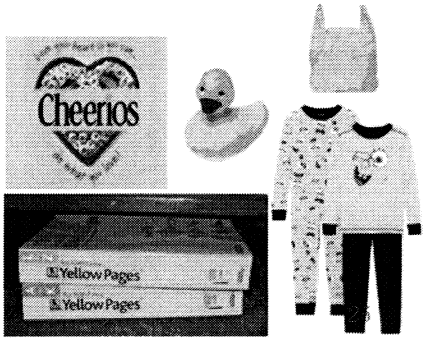
PCB concentrations in the product have to average less than 25 ppm and can be no higher than 50 ppm.

BUT, the concentrations of monochlorobiphenyls are divided by 10, and dichlorobiphenyls by 5.

(Pigment process waste is classified as hazardous waste)

Transfer of PCBs in a concentration of 50 mg/kg or over is prohibited by the Stockholm Convention on Persistent Organic Pollutants.





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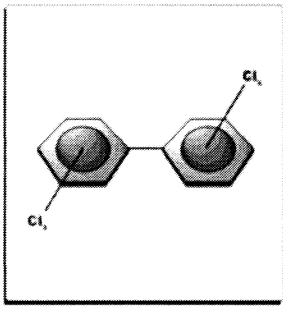
EPA method 1668A

~~EPA~~ Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS



EPA developed a new method to measure PCBs, using the new high-resolution GC/MS.

This method measured ALL of the PCB congeners, not just the ones in the Aroclors.

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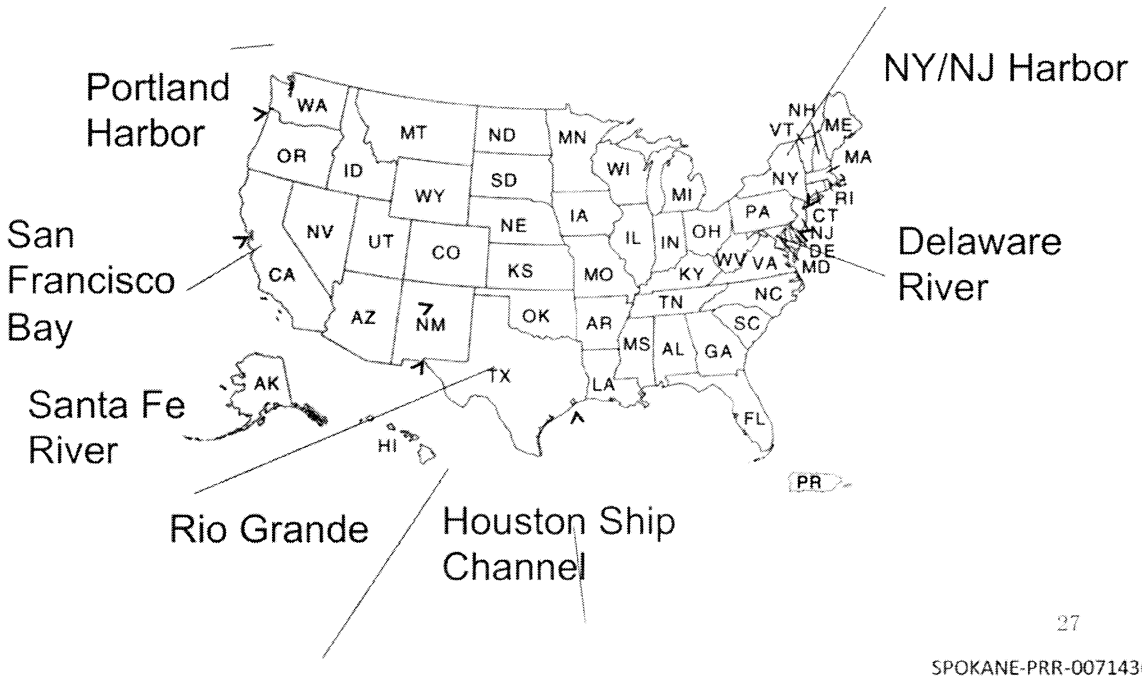
PCB 11 started showing up everywhere



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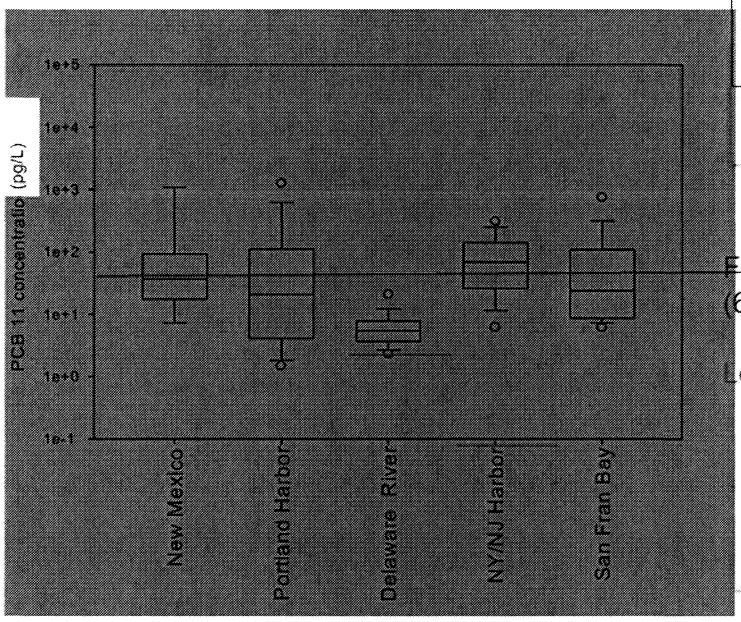
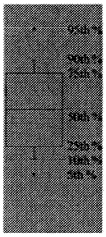
PCB 11 concentrations across US waterways



Water Quality Standards (WQS) ΣPCBs

Federal WQS (64 pg/L)

Local WQS



(Data from CARP, DRBC, SFEI, and STORET)

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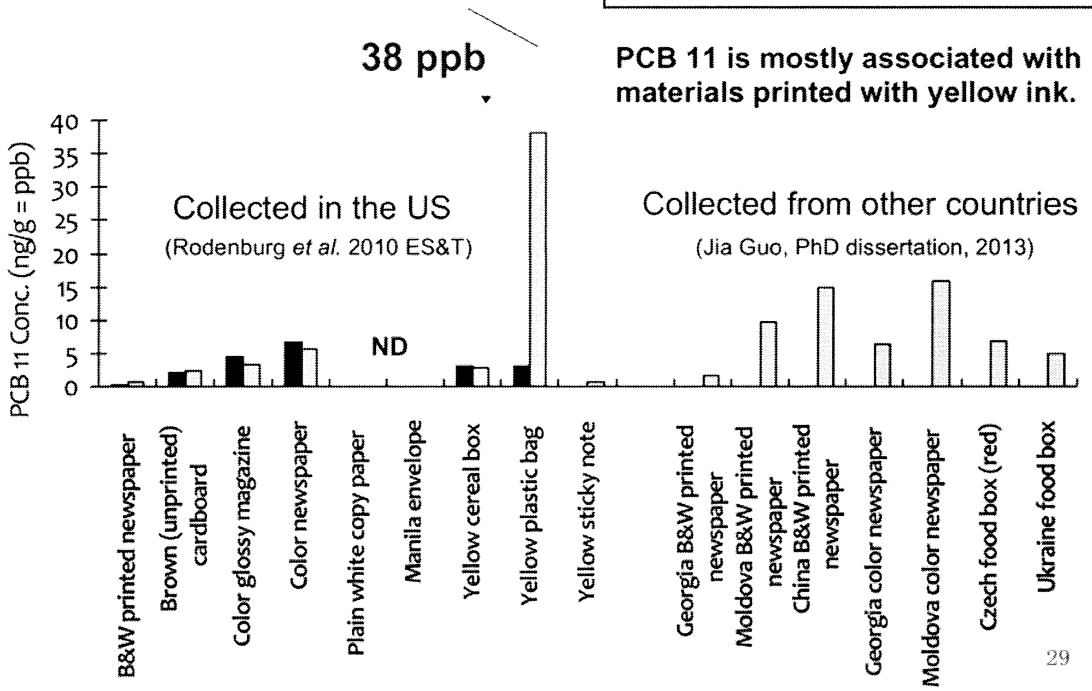
PCB 11 in Printed Materials



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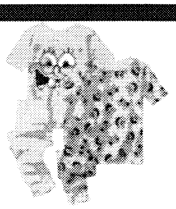
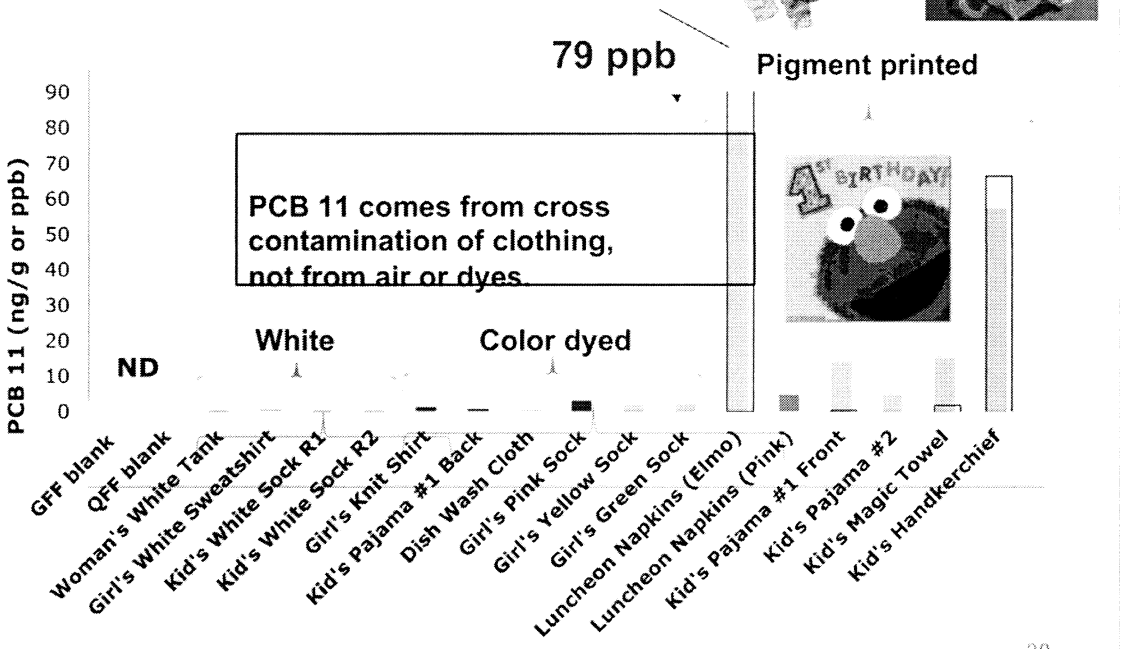
PCB 11 in Fabric Materials





(Jia Guo, PhD dissertation, 2013)

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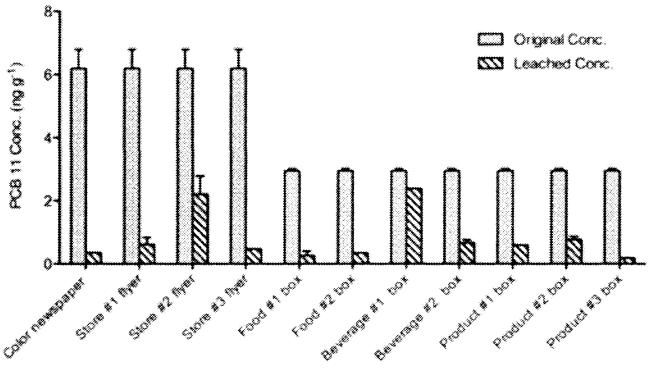
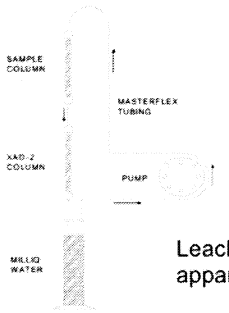
Leaching of PCB 11



6~81% PCB 11 leached after 48 h

(Jia Guo, PhD dissertation, 2013)



Leaching apparatus

A newspaper rapidly dissolving in front of my home

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Pigment industry response

ETAD

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers

Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), ETAD Position On The Presence Of Traces Of PCBs In Some Organic Pigments. **2011**.

"…PCBs are present both on the surface and in the solid pigment matrix. This incorporated PCB is unlikely to lead either to human or environmental exposure. Additionally pigments are used to colour paints, inks and plastics and are themselves incorporated into a further matrix making release improbable – until both polymeric matrix and the pigments degrade."

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Mass flow analysis of PCB 11 in the Delaware River Basin (DRB)

$$\frac{dM}{dt} = I - O - R_{tot}$$

Accumulation = 0 @ steady state

Inflow

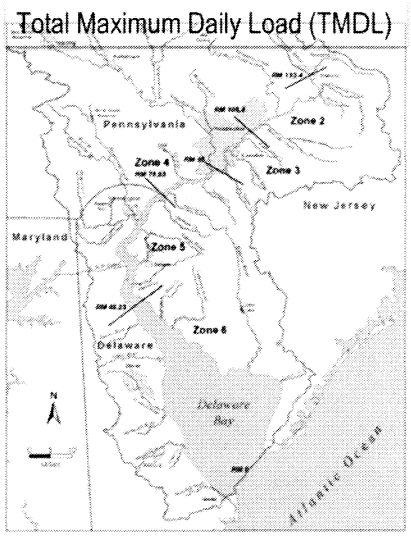
Outflow

Reaction

I>O: most PCB 11 stays in the pigment, only some gets out to environment

O>I: pigment degrades into PCB 11

(Jia Guo, PhD dissertation, 2013)



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How much PCB 11 does pigment contain?

- Measured values range widely
  - PCB 11 in printing ink = 15 ng/g = 75 ng/g in pigment
  - Max allowed by law is average of 125 ppm (ug/g)
- Pigment production = 250,000 t (Savastano, 2007)
  - Range of 5 to 7,800 kg/y PCB 11 produced!
- Can 5 kg/y be reasonable?
- NO!
  - 40-100 kg/y of PCB 11 coming out of one WWTP that treats pigment process waste in the NYC area

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How much PCB 11 enters the DRB each year?

- US consumes 20% of world pigment market (IHS, 2011)
- Assume pigment use scales by population
  - DRB = 2.7% of US population (2010 Census)

	PCB 11 in pigment	World PCB 11 production (kg/y)	PCB 11 Import to DRB (kg/y)
Low-end	75 ppb	5	**0.025**
High-end	125 ppm	7800	**42**

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How much PCB 11 exits the DRB each year?

- Using the DRBC's excellent data set, we can calculate:
  - Flow of PCB 11 out to Atlantic (0.09 kg/y)
  - Sequestration in sewage sludge (0.28 kg/y)
  - Sequestration in river sediment (0.26 kg/y)

Lower bound estimate of 0.025 kg/y into DRB is not reasonable!

- Using our Delaware Atmospheric Deposition Network (DADN) data, we can calculate:
  - Volatilization to atmosphere

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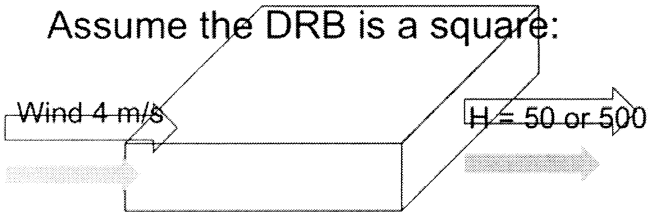
Air emissions required

Assume the DRB is a square:



W = L = 187 km

$$I = C_{ss} \cdot V \cdot (k_w + k_{tot})$$

k_w = flushing rate = 1.85 1/d

k_{tot} = reaction with hydroxyl = 0.57 1/d

C_{ss} from DADN (pg/m³)	H (m)	I (kg/y)
6	50	**7.8**
6	500	**78**
20	50	**26**
20	500	**260**

Similar to our top estimate of 42 kg/y into basin

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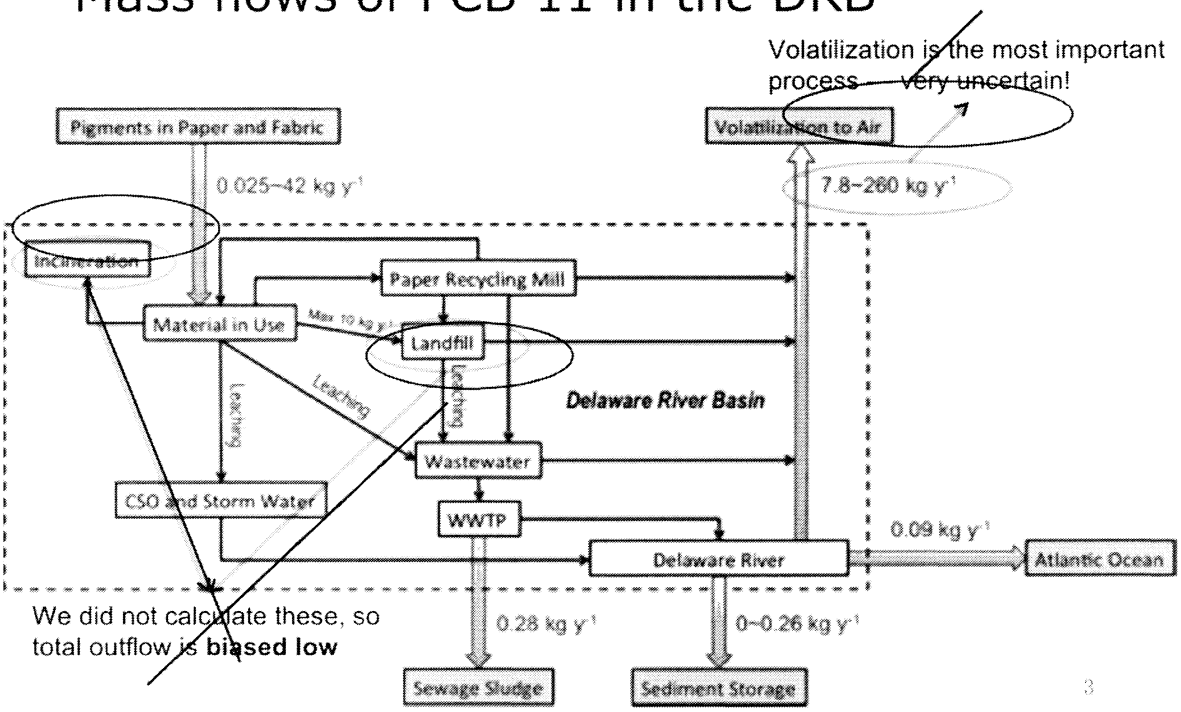
Mass flows of PCB 11 in the DRB



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No matter how you slice it…

- The lower bound estimate of PCB 11 in pigment can't be right
- The amount of PCB 11 in pigment must be close to the maximum allowed value of 125 ppm
- Virtually all of it gets out into the environment

- OR the concentration in the pigment is even higher than 125 ppm due to outsourcing of pigment production to other countries
- OR the pigment breaks down to release PCB 11
- OR we are missing some sources

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Summary

- PCB 11 and other congeners from pigments significantly contribute to water pollution
- US WQS cannot be met until these sources are reduced or eliminated
- Human exposure via clothing, napkins, and printed material is possible
- PCBs enter the wastewater stream through disposal of paper and washing of clothing
- It is important to measure most or all of the 209 PCB congeners in monitoring programs

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Environmental Council of States resolution

ECOS

- Recommends that U.S. EPA, industry, and states work together on alternatives to chlorinated solvents used in pigment and ink manufacturing to develop manufacturing processes in the next five years that do not generate PCBs, while making sure the alternatives do not themselves cause significant environmental impacts of their own;
- Supports a national approach to the problem of inadvertently-created PCBs and requests U.S. EPA commit research and development funds to establish the scope of the issue for all inadvertently-created PCBs and provide resources to establish a Design for the Environment project to reduce or eliminate inadvertently-created PCBs;
- Supports U.S. EPA's proposed rulemaking to reassess the current use authorizations for PCBs, which includes products with PCBs and products with inadvertently-generated PCBs. U.S. EPA should move forward with this rulemaking to better protect human health and the environment.
- Recommends that U.S. EPA continue its efforts to reduce PCBs and work with the international community on the elimination of PCBs.

Resolved 2012

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Acknowledgements

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new jersey department of environmental protection

Delaware River Basin Commission

Rutgers Office of Technology

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

RUTGERS
New Jersey Agricultural Experiment Station

Environmental Sciences Rutgers University

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